INVESTIGATION OF NEW COLUMN PACKINGS FOR MOLECULAR WEIGHT DETERMINATION OF HEAVY FRACTIONS BY SIZE EXCLUSION CHROMATOGRAPHY

S. Coulombe and S. Desjardins

MARCH 1987

16 pp

MICROMEDIA

ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERL 87-74(TR)

This work was supported in part by the Federal Panel on Energy R+D (PERD)

INVESTIGATION OF NEW COLUMN PACKINGS FOR MOLECULAR WEIGHT DETERMINATION OF HEAVY FRACTIONS BY SIZE EXCLUSION CHROMATOGRAPHY

S. COULOMBE* and S. DESJARDINS**

ABSTRACT

New packing materials for size exclusion chromatography columns were investigated. Polytetrafluoroethylene (Teflon) and carborundum (SiC) were selected because of their inertness and potential to avoid secondary interactions such as adsorption that would add to the size exclusion effect and make the molecular weight determination of complex samples like heavy oils and bitumen very difficult. The efficiency of columns packed with these materials was calculated and column packing procedures are discussed .

---

* Surface Science and Hydrocarbon Component Characterization Section, Fuel Characterization Research Laboratory, Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, Ottawa, K1A 0G1.

** Coop student, University of Sherbrooke.

ÉTUDE DE NOUVEAUX MATÉRIAUX DE REMPLISSAGE POUR LA DÉTERMINATION DU POIDS MOLÉCULAIRE DE FRACTIONS LOURDES PAR CHROMATOGRAPHIE D'EXCLUSION

S. COULOMBE* et S. DESJARDINS**

RÉSUMÉ

De nouveaux matériaux de remplissage pour chromatographie d'exclusion ont été étudiés. Le carborundum (SiC) et le polytétrafluoroéthylène (Teflon) ont été sélectionnés à cause de leur caractère inerte et de leur potentiel à éviter les interactions secondaires telles que l'adsorption qui s'ajoutent à l'effet d'exclusion et rendent la détermination du poids moléculaire d'échantillons complexes comme les fractions lourdes très difficile. L'efficacité des colonnes remplies avec ces matériaux est calculée et les procédures de remplissage sont discutées.

---

* Section de caractérisation des hydrocarbures et de science des surfaces, Laboratoire de recherche en caractérisation des hydrocarbures, Laboratoires de recherche sur l'énergie, CANMET, Energie, Mines et Ressources Canada, Ottawa, K1A 0G1.

** Etudiant Coop, Université de Sherbrooke.

INTRODUCTION

Size exclusion chromatography is widely used for molecular weight determination of various types of samples. This technique was developed primarily for polymers but was soon extended to high molecular fractions of oils and bitumens (1,2). However, unlike polymers, which are long chains of repeating units having more or less the same chemical properties, oil related samples are highly complex materials composed of thousands of different molecules.

In the case of polymers, the similarity of properties allows an acceptable determination because the secondary interactions that accompany the size exclusion would be approximately the same for each polymer chain. However, molecular properties are very different for the oil components. Thus, retention times do not reflect only the molecular weight or size of the molecules, and the molecular weight distribution is only indicative of the nature of the sample (3).

A series of packing materials made of polytetrafluoroethylene (PTFE or Teflon), carborundum (SiC) or various combinations of these was investigated. PTFE was selected because of its inertness and minimal interaction with oil components. Carborundum is a hard inorganic compound having a structure similar to that of diamond and is expected to have only small interactions with oil components.

EXPERIMENTAL

Experiments were performed using a Varian 5000 liquid chromatograph connected to a Varian 401 for data collection and integration. Solvent flowrate was 1 mL/min. Eluant from the column was monitored using a Waters differential refractometer R401.

Carborundum (BDH Chemicals Ltd., particle size: 180 grits, i.e., 75-89) was used as received before packing. PTFE was obtained from two sources: Chromosorb T (Teflon) 40/60 mesh size (Johns-Manville Products Corp. through Chromatographic Specialties) and Fluo-Kem dry Teflon powder (Cole-Parmer). Columns were usually dry packed. Attempts to use slurry packing technique were not successful because a good slurry could not be obtained; PTFE tends to float whereas carborundum sinks. Dichloromethane, tetrahydrofuran (THF) and toluene were purchased from Anachemia and trichloroethylene (TCE) was purchased from Caledon. These solvents were degassed before use. An on-line 5 um filter was used to prevent solid particles from entering the system.

RESULTS AND DISCUSSION

1 - Polytetrafluoroethylene (PTFE)

PTFE was selected because of its inertness and minimal interaction with the oil component. First, attempts to pack a column were done with the Teflon powder. Unfortunately, this powder was so fine that it produced a highly compressed packing making it virtually impossible to flow the solvent through. Both dry and slurry packing techniques gave the same results but the slurry technique is not practical because PTFE tends to float at the surface of the liquid.

Second, experiments were done using Chromosorb T, a gas chromatography non-polar packing based on Teflon. Initially, this material was packed as received using both dry and slurry packing. However, it was soon found that it would not pack efficiently, leaving large voids. Also since there was no back pressure on the column, it was decided to grind the Chromosorb T particles in order to achieve a compromise situation between two extremes. Results were very inconsistent as shown in Table 1. Some packings were highly compressed whereas others were very loose and gave peculiar peak shapes.

2 - Combined stationary phase (PTFE and SiC)

Results with PTFE emphasized the need to mix the PTFE material (ground Chromosorb T) with some other material that would be more rigid. Thus, if homogeneous mixing could be achieved, the packing material would not compress so easily and should be more repeatable from one column to another. Carborundum was selected because it has a structure similar to that of diamond and was expected to have minimal adsorption interaction with the sample since it does not have any pi-electrons to share with the polar molecules. In this case, slurry packing cannot be considered because of the differences of the two components.

Results from combined stationary phases are summarized in Table 2. As expected, carborundum reduced the compression of the packing material. In fact, when the proportion of carborundum is higher than 25%, there is no column back pressure. In these experiments, an artificial back pressure was created by installing a fine metering valve at the column exit in front of the detector to minimize channelling effects. Moreover, there is a definite tendency to increase efficiency with increased carborundum. This was not expected since the carborundum powder used was not particularly fine compared to chromatographic packings (<=89 um) and was expected to form large channels when packed. Table 3 gives results obtained by using several combinations of columns in order to increase the number of theoretical plates by increasing the column length and the retention time. Again, it was observed generally that the less PTFE in the columns, the higher the number of theoretical plates.

3 - Carborundum (SiC)

It was decided to try columns packed with carborundum only, although an artificial back pressure had to be created. As expected from previous results, these columns showed the highest number of theoretical plates (Table 4). However, the plate count is still far from a commercial column showing thousands of theoritical plates. It can also be seen from the experiments using the same solvent that the packing quality cannot be reproduced. This might be due to the hardness of the particles which can lead to channelling.

4 - Permeation range

The number of theoretical plates is not the only important parameter in evaluating a column in terms of applicability. One must also consider the working range of the column, in other words, what molecular weight range could be analyzed using a given column. Table 5 shows typical permeation and exclusion limits that could be observed from the calibration curves. One could observe that columns packed with carborundum show significant differences depending on the solvent used. This was not expected since this packing was very rigid and not subjected to swelling. Moreover, carborundum was expected to be free of secondary interactions related to solvent. Differences can not be explained at this point but are thought to be partly due to solvent viscosity.

Examples of typical calibration curves are shown in Fig.1 to 3. These graphs show the effect of a small plate number. We see that the difference in retention time between the light and heavy compounds is very small compared with the total analysis time. This means that in order to get a reasonable separation between components, it would be necessary to have very long columns and analysis times. Results also show that the difference in retention times for a given compound in successive runs was larger than the variation limits observed for a given column. In other words, it would be impossible to calibrate such a column properly since the retention time for a standard compound could change over the entire range of retention times observed for a complete set of standards. This problem could be overcome by having a porous packing that would increase the volume accessible to the solute molecules. However, porous PTFE would be too soft and its structure would collapse when applying pressure, and porous carborundum is not expected to be easily manufactured.

SUMMARY

Two new materials (PTFE and SiC) were investigated to determine their potential as packings for size exclusion chromatography. They were chosen because they were expected to obviate secondary interactions such as adsorption, hydrogen bonding and other solute-column interactions that would add to the size exclusion process. PTFE did not perform successfully because of the nonreproducibility of the packing quality. Combinations of PTFE/SiC were used instead to provide more reproducible packings in terms of back pressure. Pure SiC columns were also investigated. The latter gave the best results in terms of theoretical plates but the plate counts were still far from commercial columns. However, mixed columns generally provided a better molecular weight working range. An artificial back pressure had to be set up for columns packed partially or totally with carborundum to improve the repeatability. Results were not encouraging enough to pursue this approach.

REFERENCES

1. Altgelt, K.H. Gel Permeation Chromatography, in Chromatography in Petroleum Analysis. Chromatogr. Sci. Ser., 111, 287-312 (1979).

2. Albaugh, E.W. and Talarico, P.C., J. Chrom., 74, 233-53 (1972).

3. Champagne, P.J., Manolakis, E. and Ternan, M., Fuel, 64, 423-25 (1985).

LIST OF FIGURES

Fig. 1 - Permeation range for a 100% carborundum column (10.2 cm x 0.45 cm), flowrate = 1 mL/min.

Fig. 2 - Permeation range for a 10% PTFE/ 90% carborundum column (24.6 cm x 0.45 cm) followed by a 100% carborundum column (10.2 cm x 0.45 cm), flowrate = 1 mL/min.

Fig. 3 - Permeation range for a 25% PTFE/75% carborundum column, (44.8 cm x 0.45 cm), flowrate = 1 mL/min.

Table 1 - Experiments using polytetrafluoroethylene

Packing method	Dimensions (cmxcm)	Pressure (atm)	Solvent	Flowrate (mL/min)	Comments
D	15 x 0.45	306	Hexane	1.0	no inj, P too high
D	12.2 x 0.45	20 *	TCE	1.0	N=14.9 N/cm=1.22
S	?	0	CCl_4	1.0	- -
D	?	294	Hexane	1.0	no injection
D	?	86-92	Hexane	1.0	P up to 273atm
D	12.2 x 0.45	>350	TCE	1.0	no inj, P too high
D	12.6 x 0.45	52	TCE	1.0	wide peak, no calc

* Artificial pressure maintained at the column exit (before the detector)

N: Number of theoretical plates
S: Slurry packing
D: Dry packing

Table 2 - Experiments using combinations of carborundum and polytetrefluoroethylene

One-column system

Mixture	Dimensions (cm x cm)	P (atm)	Solvent	Flowrate (mL/min)	N	N/cm
A. 90% PTFE / 10% SiC						
	16.7 x 0.45	292	Hexane	0.5	Pressure too high	
B. 80% Fine PTFE / 20% SiC						
	17.6 x 0.45	124	Hexane	1.0	Packing too compressed	
C. 75% Teflon T / 25% SiC						
	15.0 x 0.45	0	Hexane	1.0	4.8	0.32
D. 70% Teflon T / 30% SiC						
	20.1 x 0.45	26	TCE	0.5	21.0	1.05
E. 50% Teflon T / 50% SiC						
	12.2 x 0.45	22*	TCE	1.0	46.0	3.77
F. 25% Teflon T / 75% SiC			(ground for 5 s)			
	17.4 x 0.45	0	Toluene	1.0	91.5	5.3
	30.2 x 0.45	26*	TCE	1.0	82.5	2.73
	44.8 x 0.45	74-80*	Toluene	1.0	141.7	3.16
	90.0 x 0.45	78-80*	Toluene	1.0	202.8	2.25
	56.0 x 0.7	0	Toluene	1.0	330.1	5.89
	40.0 x 0.45	20-24*	TCE	1.0	167.2	4.18
	44.8 x 0.45	4	TCE	1.0	7.1	0.16
G. 10% Teflon T / 90% SiC						
	24.8 x 0.45	24*	TCE	1.0	337.7	13.62
	24.8 x 0.45	30*	Toluene	1.0	331.2	13.35

* Artificial pressure maintained at the column exit (before the detector)

P: Pressure
N: Number of theoretical plates

Table 3 - Experiments using combinations of carborundum and polytetrafluoroethylene

Two-column system

Columns	Dimensions (cm x cm)	P (atm)	Solvent	Flowrate (mL/min)	N	N/cm
A. 100% SiC + 100% Teflon T						
	10.2 x 0.45 +12.2 x 0.45	48	THF	1.0	18.4	0.82
B. 50% Teflon T / 50% SiC + 100% SiC						
	12.2 x 0.45 +10.2 x 0.45	26*	TCE	1.0	115.7	5.16
C. 25% Teflon T / 75% SiC (ground for 5 sec) + 100% SiC						
	17.4 x 0.45	28*	Toluene	1.0	92.1	3.34
D. 100% SiC + 25% Teflon T / 75% SiC						
	10.2 x 0.45 +17.4 x 0.45	34*	CH_2Cl_2	1.0	119.6	4.33
	idem	36-40*	THF	1.0	64.5	2.34
E. 10% Teflon T / 90% SiC + 100% SiC						
	24.8 x 0.45 +10.2 x 0.45	46*	THF	1.0	730.1	20.86

* Artificial pressure maintained at the column exit (before the detector)

N: Number of theoretical plates

Table 4 - Experiments using carborundum

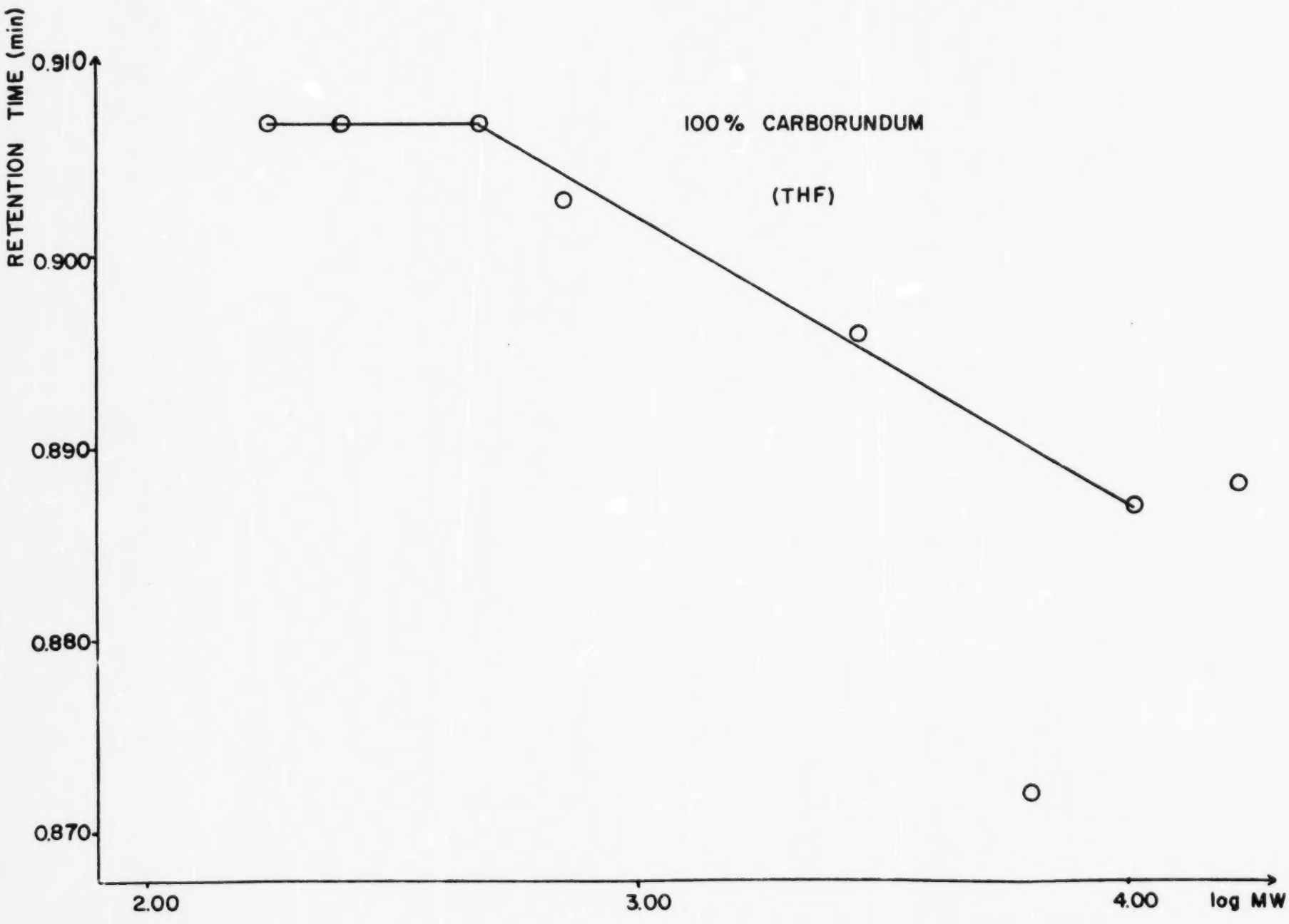
Dimensions (cm x cm)	Pressure (atm)	Solvent	Flowrate (mL/min)	N	N/cm
20.2 x 0.45	0	Toluene	1.0	775.8	38.40
10.2 x 0.45	30-32*	Toluene	1.0	251	24.6
10.2 x 0.45	40*	THF	1.0	205.2	20.12
10.2 x 0.45	28-52*	CH_2Cl_2	1.0	268.9	26.36
10.2 x 0.45	20*	TCE	1.0	247.6	24.28
10.2 x 0.45	4	TCE	1.0	316.6	31.04
13.2 x 0.45	8*	TCE	1.0	38.7	2.93

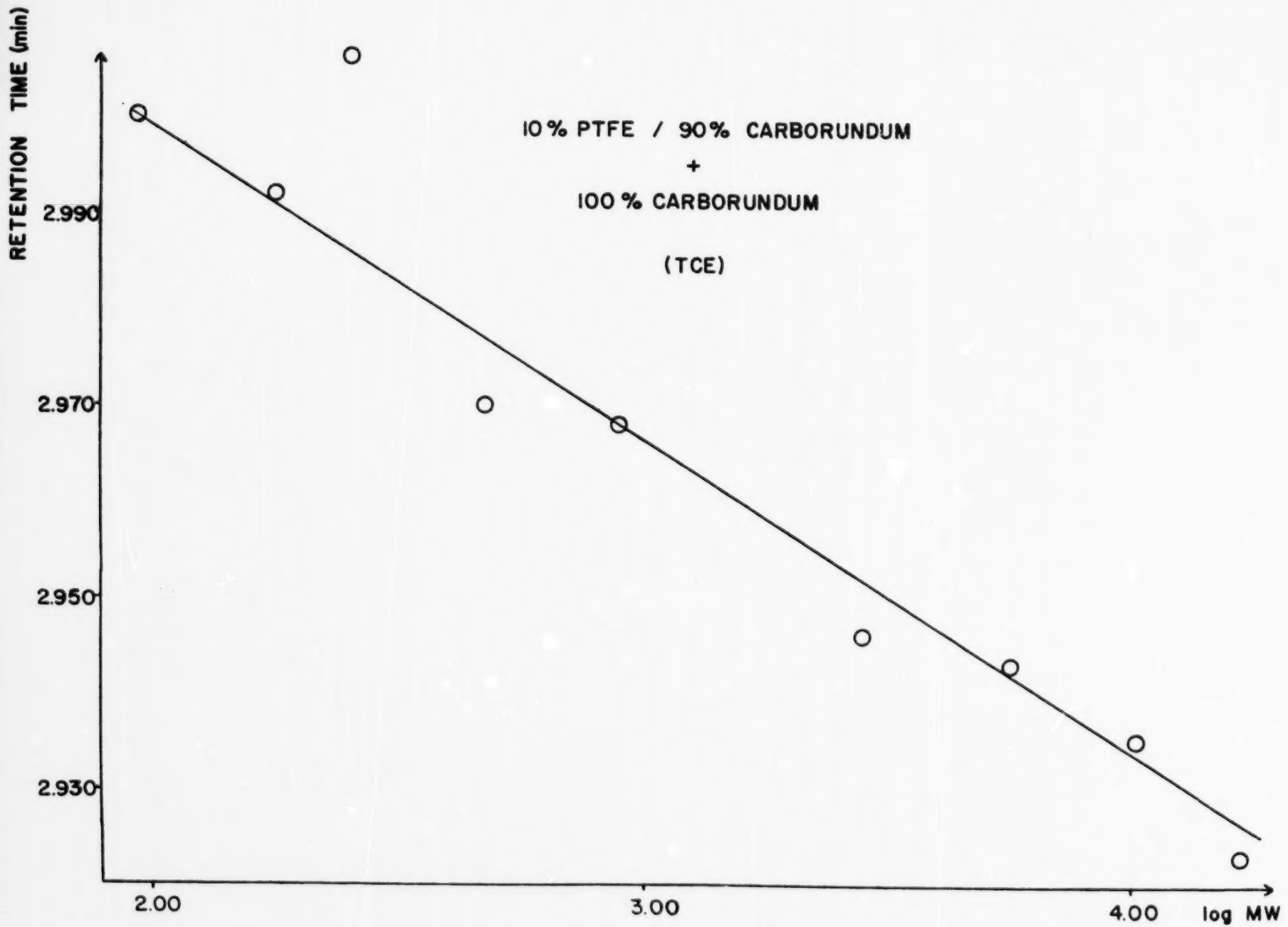
* Artificial pressure maintained at the column exit (before the detector)

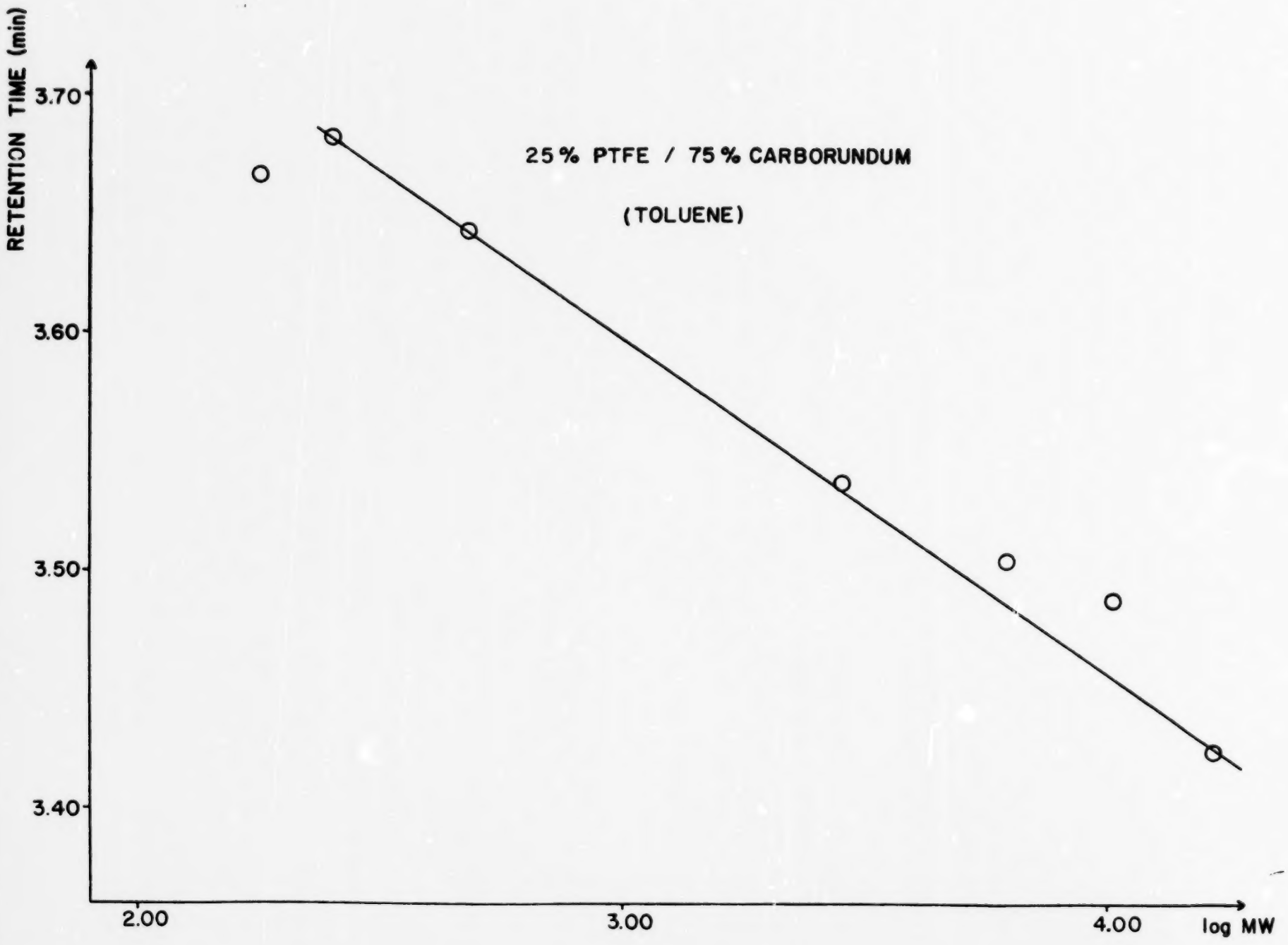
N: Number of theoretical plates

Table 5 - Typical permeation ranges of PTFE, PTFE/SiC and SiC columns

Packing	Solvent	Molecular weight limits
SiC	Toluene	0 - 250
SiC	THF	500 - 10000
SiC	TCE	0 - 500
25% PTFE/75% SiC	Toluene	300 - 10000
10% PTFE/90% SiC	TCE	300 - 6000
10% PTFE/90% SiC + 100% SiC	TCE	100 - 15000
25% PTFE/75% SiC + 100% SiC	Toluene	250 - 15000
100% SiC + 25% PTFE/75% SiC	THF	250 - 10000
10% PTFE/90% SiC + 100% SiC	TCE	250 - 15000


RETENTION TIME (min)
0.910
0.900
0.890
0.880
0.870
100% CARBORUNDUM
(THF)
2.00
3.00
4.00
log MW


RETENTION TIME (min)
2.990
2.970
2.950
2.930
10 % PTFE / 90% CARBORUNDUM
+
100 % CARBORUNDUM
(TCE)
2.00
3.00
4.00
log MW


RETENTION TIME (min)
3.70
3.60
3.50
3.40
25 % PTFE / 75 % CARBORUNDUM
(TOLUENE)
2.00
3.00
4.00
log MW